

1. Kinetics

Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction, $aA + bB \rightarrow$ products, the generalised rate equation is: $r = k[A]^m[B]^n$

r is used as symbol for rate

The unit of r is usually $\text{mol dm}^{-3}\text{s}^{-1}$

m, n are called **reaction orders**

Orders are usually integers 0,1,2

0 means the reaction is zero order with respect to that reactant

1 means first order

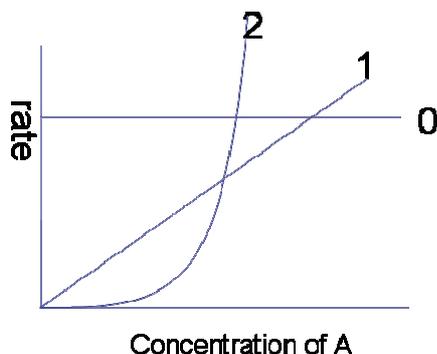
2 means second order

The square brackets **[A]** means the concentration of A (unit mol dm^{-3})

k is called the **rate constant**

NOTE: the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

The **total order** for a reaction is worked out by adding all the individual orders together ($m+n$)



For zero order: the concentration of A has no effect on the rate of reaction $r = k[A]^0 = k$

For first order: the rate of reaction is directly proportional to the concentration of A $r = k[A]^1$

For second order: the rate of reaction is proportional to the concentration of A squared $r = k[A]^2$

The rate constant (k)

1. The units of k depend on the overall order of reaction. It must be worked out from the rate equation
2. The value of k is independent of concentration and time. It is constant at a fixed temperature.
3. The value of k refers to a specific temperature and it **increases** if we **increase temperature**

For a 1st order overall reaction the unit of k is s^{-1}

For a 2nd order overall reaction the unit of k is $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

For a 3rd order overall reaction the unit of k is $\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

Example (first order overall)

Rate = $k[A][B]^0$ $m = 1$ and $n = 0$

- reaction is first order in A and zero order in B

- overall order = $1 + 0 = 1$

- usually written: Rate = $k[A]$

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

Calculating units of k

1. Rearrange rate equation to give k as subject

2. Insert units and cancel

$$k = \frac{\text{Rate}}{[A]}$$

$$k = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$$

Unit of $k = \text{s}^{-1}$

Example: Write rate equation for reaction between A and B where A is 1st order and B is 2nd order.

$$r = k[A][B]^2 \quad \text{overall order is 3}$$

Calculate the unit of k

1. Rearrange rate equation to give k as subject

$$k = \frac{\text{Rate}}{[A][B]^2}$$

2. Insert units and cancel

$$k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3} \cdot (\text{mol dm}^{-3})^2}$$

3. Simplify fraction

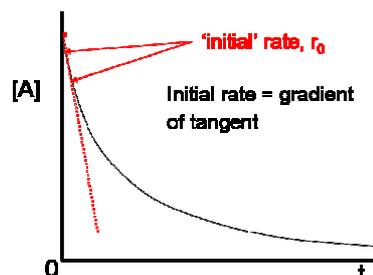
$$k = \frac{\text{s}^{-1}}{\text{mol}^2 \text{dm}^{-6}}$$

$$\text{Unit of } k = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

Working out orders from experimental initial rate data

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time. This data is normally presented in a table.



Example: work out the rate equation for the following reaction, $A + B + 2C \rightarrow D + 2E$, using the initial rate data in the table

| Experiment | [A] mol dm ⁻³ | [B] mol dm ⁻³ | [C] mol dm ⁻³ | Rate mol dm ⁻³ s ⁻¹ |
|------------|-----------------------------|-----------------------------|-----------------------------|--|
| 1 | 0.1 | 0.5 | 0.25 | 0.1 |
| 2 | 0.2 | 0.5 | 0.25 | 0.2 |
| 3 | 0.1 | 1.0 | 0.25 | 0.4 |
| 4 | 0.1 | 0.5 | 0.5 | 0.1 |

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A compare between experiments **1 and 2**

For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3** :

As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**.

Therefore the order with respect to **B is 2nd order**

For reactant C compare between experiments **1 and 4** :

As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**.

Therefore the order with respect to C is zero order

The overall rate equation is $r = k [A] [B]^2$

The reaction is 3rd order overall and the unit of the rate constant = mol⁻²dm⁶s⁻¹

Working out orders when two reactant concentrations are changed simultaneously

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes are multiplied together.

In a reaction where the rate equation is $r = k [A] [B]^2$

If the [A] is x2 that rate would **x2**

If the [B] is x3 that rate would $x3^2 = \mathbf{x9}$

If these changes happened at the same time then the rate would $x2 \times x9 = \mathbf{x18}$

Example work out the rate equation for the reaction, between X and Y, using the initial rate data in the table

| Experiment | Initial concentration of X/ mol dm ⁻³ | Initial concentration of Y/ mol dm ⁻³ | Initial rate/ mol dm ⁻³ s ⁻¹ |
|------------|--|--|--|
| 1 | 0.05 | 0.1 | 0.15×10^{-6} |
| 2 | 0.10 | 0.1 | 0.30×10^{-6} |
| 3 | 0.20 | 0.2 | 2.40×10^{-6} |

For reactant X compare between experiments **1 and 2**

For reactant X as the concentration **doubles** (Y staying constant) so does the rate. Therefore the order with respect to reactant **X is first order**

Comparing between experiments 2 and 3 :

Both **X and Y double** and the **rate goes up by 8**

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

Y must be second order

The overall rate equation is $r = k [X] [Y]^2$

The reaction is 3rd order overall and the unit of the rate constant = mol⁻²dm⁶s⁻¹

Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

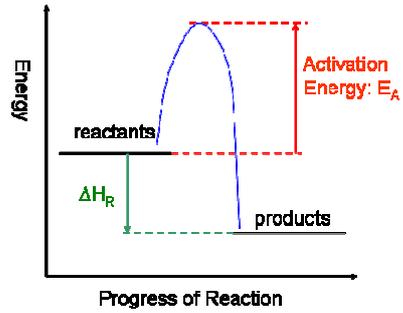
$$r = k [X] [Y]^2 \longrightarrow k = \frac{r}{[A] [B]^2} \quad k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} \quad k = \mathbf{3.0 \times 10^{-4} \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}}$$

Remember k is the same for all experiments done at the same temperature.

Increasing the temperature increases the value of the rate constant k

Revision of AS kinetics Maxwell Boltzmann Distribution

The **Activation Energy** is defined as the minimum energy which particles need to collide to start a reaction



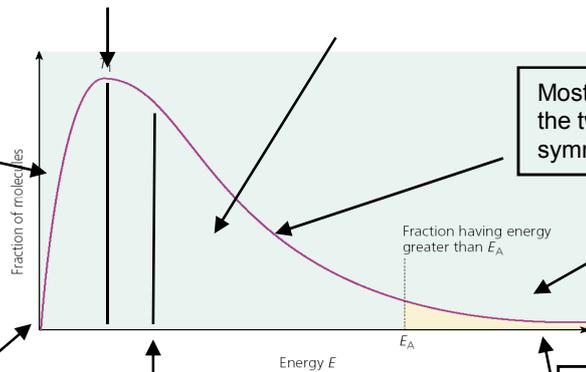
The Maxwell-Boltzmann energy distribution shows the spread of energies that molecules of a gas or liquid have at a particular temperature

Learn this curve carefully

E_{mp} this is the most probable energy (not the same as mean energy)

The area under the curve represents the total number of particles present

The energy distribution should go through the origin because there are no molecules with no energy



Most molecules have energies between the two extremes but the distribution is not symmetrical (normal)

Only a few particles have energy greater than the E_A

A few have low energies because collisions cause some particles to slow down

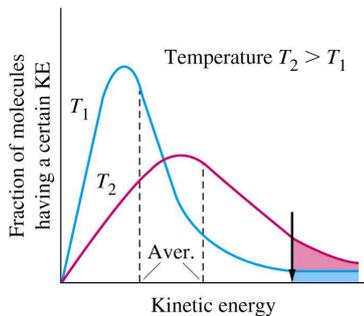
The mean energy of the particles is not at the peak of the curve

The energy distribution should never meet the x axis, as there is no maximum energy for molecules

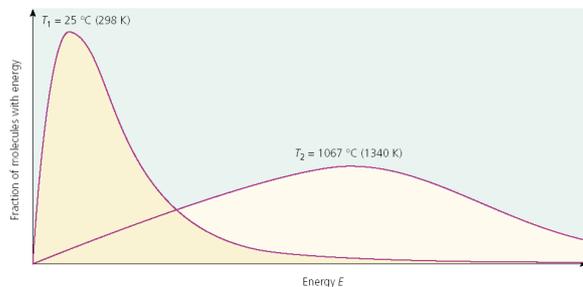
Increasing Temperature

As the temperature increases the distribution shifts towards having more molecules with higher energies

At higher temperatures the energy of the particles increases. They collide more frequently and more often with energy greater than the activation energy. More collisions result in a reaction



Both the E_{mo} and mean energy shift to high energy values



The total area under the curve should remain constant because the total number of particles is constant

At higher temperatures the molecules have a wider range of energies than at lower temperatures.

As the temperature increases, the graphs show that a bigger proportion of particles have **energy greater than the activation energy**, so the frequency of successful collisions increases

Increasing the temperature increases the value of the rate constant k

Rate Equations and mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

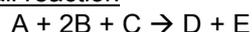
Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. **The slowest step is called the rate-determining step.**

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.

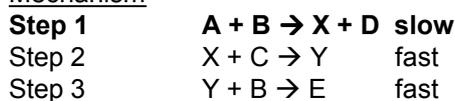
e.g. 0 moles of A in slow step will mean A is zero order.

Example 1

overall reaction



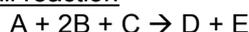
Mechanism



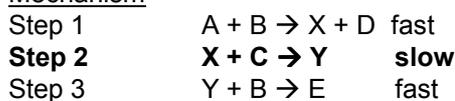
$$r = k [A]^1 [B]^1 [C]^0$$

Example 2

overall reaction



Mechanism



$$r = k [X]^1 [C]^1$$

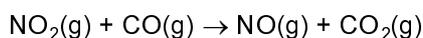
The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step



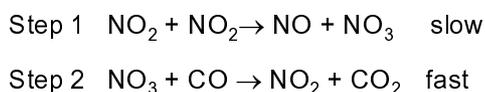
$$r = k [A]^1 [B]^1 [C]^1$$

Example 3

Overall Reaction



Mechanism:



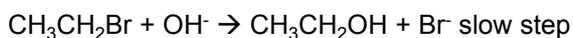
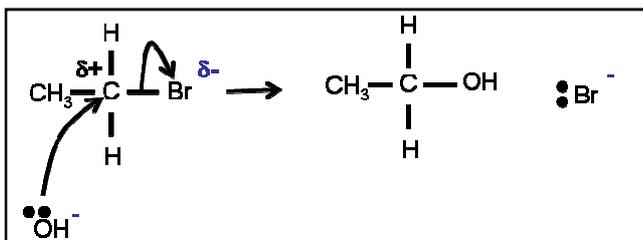
• NO_3 is a reaction intermediate

$$r = k [NO_2]^2$$

Example 4: S_N1 or S_N2 ? You don't need to remember the details here.

Remember the nucleophilic substitution reaction of haloalkanes and hydroxide ions.

This is a one step mechanism



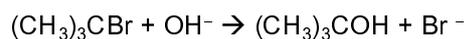
The rate equation is

$$r = k [CH_3CH_2Br] [OH^-]$$

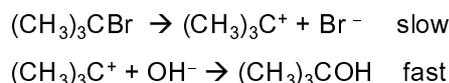
This is called S_N2 .
Substitution, **N**ucleophilic,
2 molecules in rate
determining step

The same reaction can also occur via a different mechanism

Overall Reaction



Mechanism:



The rate equation is

$$r = k [(CH_3)_3CBr]$$

This is called S_N1 .
Substitution, **N**ucleophilic,
1 molecule in rate
determining step